Silicon-Induced Layer-by-Layer Growth of GaN

Improvements in silicon-doped GaN-based devices can only be realized through a fundamental understanding of their materials. We have used x-ray scattering measurements to investigate the growth behavior of silicon-doped GaN films as they are formed. The change in the growth mode of GaN from step-flow to layer-to-layer growth is determined by silicon pinning.

Growth of nitride-based devices has recently revolutionized the field of solid-state light emitters by enabling the fabrication of blue, green, and ultraviolet light-emitting diodes (LEDs) and laser diodes (LDs). Blue LDs allow for higher density storage (4-6 times that of the digital versatile disk) due to the shorter wavelength of blue (450 nm) compared to red (650 nm) light. Blue and green nitride-based LEDs combine with amber and red phosphide-based LEDs to provide the full color spectrum and thus allow use of LEDs for applications such as multicolor displays and backlighting for flat-panel displays. In addition, the efficiency of current LEDs exceeds that of conventional light sources [1]. The energy savings are magnified for single-wavelength light applications, such as traffic lights, where the white light emitted from conventional bulbs is filtered by a colored lens. Despite this technology breakthrough, there is still much potential for advancement. The quantum efficiency, lifetime, and power density in current devices are far from their theoretical maxima and are primarily limited by material quality. A fundamental understanding of the growth of GaN is therefore essential for further improvement.

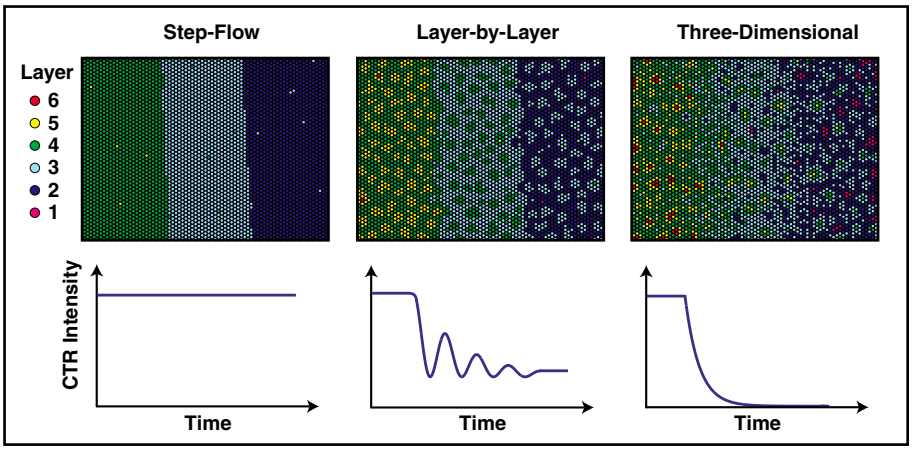

FIG. 1. Schematic of atomic-scale surface morphology during step-flow, layer-by-layer, and three-dimensional growth modes, and the corresponding behavior of the CTR intensity when growth is initiated.

Silicon is an important n-type dopant in GaN devices. Incorporation of silicon of more than 10^{19} cm^{-2} is desired in order to achieve sufficient conductivity in the contact layer. However, it remains difficult to grow micrometer-thick, high-quality GaN at these high doping levels. The films either crack after cooling to room temperature due to incorporated tensile stresses [2], or the surfaces rapidly roughen [3] and are therefore unsuited for subsequent growth of the light-emitting active layer.

GaN is typically grown by metal organic chemical vapor deposition (MOCVD), where gases in the vicinity of a heated substrate decompose and react to form an epitaxial film. Due to the chemically reactive environment and near-atmospheric pressure of MOCVD, the use of conventional *in situ* surface science characterization tools (e.g., electron diffraction) is not feasible. Our current knowledge of the atomic-scale nature of nitride growth by MOCVD is thus primarily inferred from *ex situ* studies of surface morphology and film microstructure.

Synchrotron radiation can penetrate the reactive MOCVD environment and nondestructively probe the sample during growth. Grazing-incidence x-ray scattering (GIXS), in which the x-rays are incident on the surface at a very shallow angle, provides special sensitivity to the surface structure. By monitoring features in the scattering known as "crystal truncation rods" (CTRs), the homoepitaxial growth modes can be observed. As shown in Fig. 1, the time dependence of the CTR intensity during growth is characteristic of the growth mode [4]. For example, for layer-by-layer growth, where islands subsequently nucleate and coalesce, the CTR intensity oscillates with each monolayer of growth, analogous to RHEED oscillations. For step-flow growth, where the atoms attach at the step edges and the surface morphology is independent of time, the CTR intensity remains constant, whereas for three-dimensional growth, where the surface rapidly roughens, the CTR intensity drops rapidly. Since only a few monolayers of growth are needed to determine the growth mode using this technique, the surface can easily be recovered by growth of undoped material at high temperature in preparation for subsequent growth. This allows us to explore a wide range of process parameters (such as doping levels, temperature, pressure, and growth rate) on a single sample and thereby rapidly obtain information about the crystal growth mechanisms.

Experiments were performed at a facility for *in situ* studies of MOCVD at the Basic Energy Sciences Synchrotron Radiation Center (BESSRC-CAT) undulator beamline 12-ID-D at the Advanced Photon Source. Growth experiments used a vertical flow chamber with quartz windows mounted on a diffractometer [5]. X-ray scattering was performed using 24 keV photons. Trimethylgallium (TMG) and ammonia are used as precursors for GaN growth, and disilane (S_2H_6) is the precursor used for silicon doping. The carrier gas is nitrogen. Studies of the effect of silicon doping were carried out on ~2-μm-thick GaN(001) films grown onto sapphire substrates at the University of California, Santa Barbara. Typical conditions were a total pressure of 200 torr, an NH_3 flow of 1.2 slpm out of a total flow of 6.3 slpm, and a TMG flow of 0.78 μmol/min during growth.

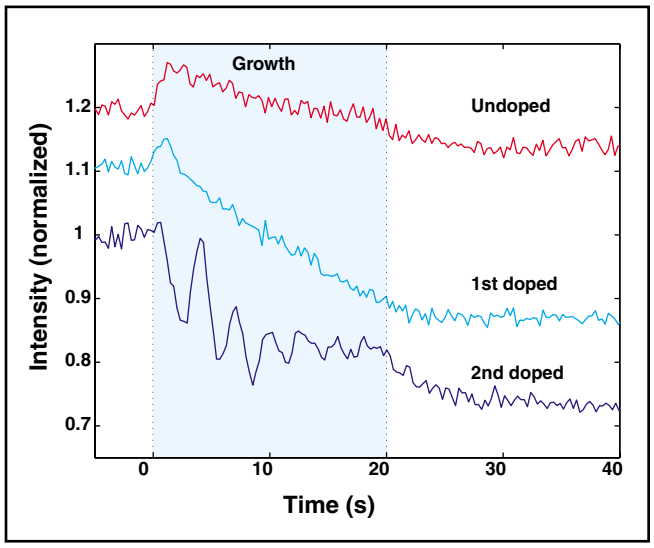

FIG. 2. Time dependence of the CTR intensity during undoped and Si-doped growth of 6.5 monolayers at 810°C. The growth occurs at times represented by the blue area. The curves are normalized to the initial intensity and are offset for clarity.

Our initial studies of Si-doped GaN growth revealed that the growth behavior depended as much on the time between growth pulses as it did on the concentration of silicon [6,7]. This is shown in Fig. 2, where the growth of undoped GaN (6.5 monolayers in 20 s at 810°C) as well as the first and second silicon-doped growths are shown. The concentration of silicon in the two doped growth pulses was 3.5×10^{20} cm^{-3}. The growth mode of the first doped growth is very similar to that of undoped growth (i.e., step flow), although more roughening is occurring as indicated by the decay in the CTR intensity. However, growth of the second pulse gives rise to oscillations in the CTR intensity, indicating layer-by-layer growth. To explore this further, we grew a series of two pulses of doped growth onto an undoped surface, varying the anneal time between the pulses (Fig. 3a). For an anneal time of 12 s, there are only weak oscillations. However, as the anneal time increases, the depth of the oscillations increases, suggesting that the growth behavior becomes predominantly layer by layer.

We also studied the effect of dosing the GaN surface with silicon prior to a growth pulse (Fig. 3b). As the dose is increased from 0 to 0.077 monolayer of silicon, the subsequent growth mode changes drastically from step-flow to layer-by-layer growth.

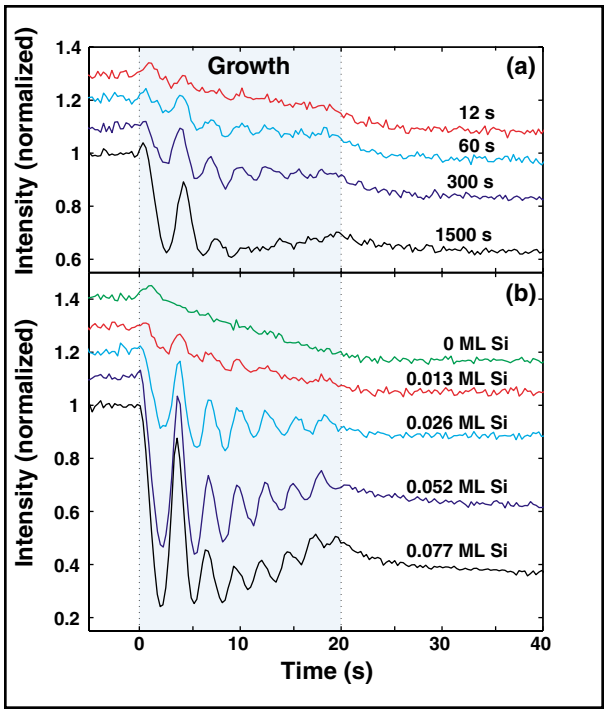

FIG. 3. Evolution of CTR intensity during (a) the second growth pulse for various anneal times between two doped growths; (b) doped growth after various surface doses of Si. Intensities are normalized to the value prior to initiation of the growth pulse and are offset for clarity.

Thus, either depositing silicon on an undoped GaN surface or annealing a Si-doped GaN film causes subsequent growth to be dominated by island nucleation and coalescence (layer-by-layer growth).

These studies suggest that Si is diffusing from the bulk to the surface during annealing of a doped film and that a few percent coverage of the surface by Si produces layer-by-layer growth, which results in rougher film surfaces. A transition from step-flow to layer-by-layer growth can be explained by silicon pinning the steps on the surface. This increases the probability that atoms arriving on the surface during growth will nucleate and form new islands [8]. We saw this effect at all temperatures explored [6], including the typical growth temperatures (> 1000ºC) of n-contact layers. Thus, using *in situ* x-ray scattering, we have shown that high concentrations of silicon cause a change in the crystal growth mode, which can have severe implications for nitride devices.

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